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**HOT-SALT STRESS-CORROSION OF TITANIUM ALLOYS
AS RELATED TO TURBINE ENGINE OPERATION**

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Introduction

Numerous laboratory investigations (1) have demonstrated that titanium alloys are susceptible to embrittlement and cracking while being stressed at elevated temperatures in the presence of halides. This phenomenon has been termed hot-salt stress-corrosion and is of interest because of the extensive utilization of titanium alloys in gas-turbine engines. Conditions of stress, temperature, and salt-air environment which result in stress-corrosion in the laboratory can be experienced by compressor components of current engines (2,3). Since advanced engine designs specify that titanium alloys operate at even higher stresses and temperatures than in current engines, there is concern that hot-salt stress-corrosion might become the limiting factor in the use of titanium alloys.

Although there have been instances of hot-salt stress-corrosion cracking during titanium alloy processing and during engine test stand operation (4), there have not yet been any documented in-flight failures that could conclusively be attributed to hot-salt stress-corrosion cracking. The objective of this research program at NASA Lewis Research Center has been to rationalize this lack of service failures and to determine what the future expectations may be.

One of the preferred laboratory test techniques for determining susceptibility to hot-salt stress-corrosion involves subjecting salt-coated titanium alloy specimens to static loads in the temperature range 250° to 500° C. The specimens are generally

exposed for 100 hours and then examined for evidence of corrosion or cracking and they may be subjected to mechanical testing to determine residual ductility. The results are then interpreted on a stress-corrosion or no-stress-corrosion basis. Thus, the boundary line separating regions of cracking from no cracking or embrittlement from nonembrittlement on a plot of exposure stress against exposure temperature has been termed the threshold curve for hot-salt stress-corrosion.

In an effort to simulate typical compressor operating conditions of current turbine engines, special test facilities were designed. Air velocity, air pressure, air dewpoint, salt deposition temperature, salt concentration, and specimen surface condition were systematically controlled and their influence on hot-salt stress-corrosion evaluated. The influence of both continuous and cyclic stress-temperature exposures was determined. The relative susceptibility of a variety of titanium alloys in commonly used heat-treated conditions was determined. The effects of both environmental and material variables were used to interpret the behavior of titanium alloys under hot-salt stress-corrosion conditions found in jet engines and to appraise their future potential under such conditions.

Experimental Procedure

The compositions, heat treatments, and resultant microstructures of the alloys used in this investigation are listed in Tables I and II. Alloy vendors, heat numbers, bar sizes, mechanical properties, photomicrographs and details of the hydrogen analysis procedures of stress-corroded specimens are published elsewhere (5). Tubular titanium alloy specimens were tested with both as-machined and chemically-milled (stress-relieved) surface conditions (6).

The usual test procedure consisted of precoating the bore of the tubular specimens at 200° C with sodium chloride to an average concentration of 0.1 mg/cm². Specimens were then exposed for 96 hours in the temperature range 320° to 480° C at stresses of from 70 to 830 MN/m² in a dynamic air apparatus which permitted Mach 0.7 air to pass through the bore of the specimens. Subsequent to stress-corrosion exposure, specimens were tensile tested at room temperature at a constant crosshead speed of 0.01 cm/min to determine residual ductility. The fracture surface of each specimen was also examined for evidence of stress-corrosion cracking. Both embrittlement and crack threshold curves were usually determined.

Results and Discussion

The results of this investigation demonstrate that the major variables that influence susceptibility of titanium alloys to hot-salt stress-corrosion are: 1. alloy processing conditions and heat treating variations; 2. specimen surface condition; and 3. cyclic exposure conditions. The dynamic air environment typical of that encountered in the compressor of current gas-turbine engines does not exert a major influence on susceptibility to hot-salt stress-corrosion. Specifically, environmental variables such as air velocity (up to Mach 0.7), air pressure (up to 52 psia), air dewpoint (-84° to 4° C), salt concentration (0.03 to 0.3 mg/cm²), and salt deposition temperature (200° to 430° C) exert only minor influences on stress-corrosion susceptibility (6). It is possible that air velocities greater than Mach 0.7 or an impinging airflow might result in more pronounced effects.

Alloy Processing and Heat Treating Conditions

The relative susceptibility to cracking of the alloys in the various heat-treated conditions listed in Table II is shown in figure 1. The 5621S alloy exhibited the widest range of susceptibility of all the alloys tested. The 5621S (1) condition ($\alpha + \beta$ roll, $\alpha + \beta$ anneal) exhibited the best resistance to cracking. The 5621S (2A) condition ($\alpha + \beta$ roll, β anneal) had intermediate resistance while the 5621S (2B) (β roll, β anneal) and (2C) (β roll, β anneal, $\alpha + \beta$ anneal) conditions were extremely susceptible to cracking. The 679, 6242, and 64 alloys exhibited good resistance to cracking in each of the heat-treated conditions tested. The susceptibility of the 811 alloy varied markedly for the four conditions studied. For example, the triplex condition resulted in good resistance, the duplex and mill annealed/air cooled conditions had fair resistance and the mill annealed/furnace cooled condition had very poor resistance to cracking.

It is tempting to rationalize the relative susceptibility of the alloys studied in this investigation according to chemical composition. Specifically, several previous investigators have ranked the stress-corrosion susceptibility of titanium alloys according to aluminum, aluminum plus oxygen, and beta stabilizer content. The lower the Al and/or O₂ concentration, or the higher the beta stabilizer content, the more resistant to stress corrosion the alloy was found to be (5). Although these schemes may have merit, the results obtained in this investigation which demonstrate the wide range of susceptibility shown by a single alloy (e.g., 811 and 5621S) indicate that caution must be exercised when ranking alloys by composition. Specifically, the dramatic influence of processing variables, subsequent heat treatments, and the resulting microstructural variations must be considered.

Although a full evaluation of microstructural variations was beyond the scope of our investigation (5), a few trends can be determined from the results obtained for the 811 and 5621S alloys.

1. A microstructure consisting of equiaxed primary alpha in a continuous transformed beta matrix is most resistant to hot-salt stress-corrosion cracking (811 triplex and 5621S (1) processed high in the alpha plus beta phase field).
2. A microstructure consisting of equiaxed beta in a continuous matrix of primary alpha exhibits intermediate resistance to stress-corrosion (811 mill anneal/air cool and 811 duplex processed low in the alpha plus beta phase field).
3. An acicular transformed beta structure is least resistant to cracking (5621S (2B) and (2C) processed above the beta transus).
4. Alloys with more than about 6 percent aluminum exhibit extreme susceptibility to stress-corrosion if heat treated under conditions likely to form Ti_3Al . This ordered phase results from slow cooling through or extended annealing in the temperature range 500° to 600° (811 mill annealed/furnace cooled).

The data presented in figure 1 and Table II also suggest that the 679, 6242, and 64 alloys are not as sensitive to microstructural variations as are the 811 and 5621S alloys. The 679, 6242, and 64 alloys with microstructures consisting of both continuous and discontinuous alpha phase exhibited equally good resistance to stress-corrosion cracking. However, it has been demonstrated that certain processing and heat-treating conditions, heat-to-heat variations, and nonuniformly worked structures can influence the stress-corrosion susceptibility of these apparently resistant alloys. The most commonly used service alloy is the 64, whose threshold stresses, shown in figure 1, are greater than design stresses (2). Recently, investigators (7) have shown that the threshold stress of mill annealed 64 alloy decreased about 35 percent after annealing above the beta transus. They also reported heat-to-heat variations in threshold stress of up to 100 percent for the 64 and 6242 alloys. In addition, unpublished research by the author indicates that 6242 in banded plate is more susceptible to stress-corrosion than is uniformly worked bar stock.

Specimen Surface Condition

The influence of specimen surface condition on susceptibility to hot-salt stress-corrosion was evaluated by determining threshold curves with specimens in two conditions: as-machined and chemically milled. Crack threshold curves determined in the dynamic air environment for the 811 and 64 alloys are shown in figure 2.

It is evident that crack threshold curves exhibited by chemically milled specimens are substantially below the threshold curves exhibited by specimens in the as-machined condition. For at least one exposure temperature for each of these three alloys, the difference between the threshold stresses was 200 to 400 MN/m².

As demonstrated by these results, specimen surface condition can exert a significant influence on susceptibility to stress-corrosion. The fact that most threshold curves occurred at lower stresses for chemically milled (stress-relieved) than for as-machined specimens indicates that the residual surface stresses resulting from machining the bore of the tubular specimens were compressive. This assumption is consistent with the type of machining operation involved and with the results of other investigations (8) which demonstrated that mechanically induced (glass-bead and shot peening or vibratory cleaning techniques) residual compressive stresses were effective in preventing or alleviating hot-salt stress-corrosion. Of course, some types of machining operations could introduce residual tensile stresses in specimens of different configurations. In those instances, threshold curves for specimens with residual tensile surface stresses could be expected to occur at lower stress levels than if the same specimens were in a stress-relieved condition.

In summary, both the results of this investigation and those reported in the literature indicate that specimen surface condition can exert a major influence on susceptibility of titanium alloys to hot-salt stress-corrosion. Residual compressive stresses resulting from either machining or peening can protect titanium alloys from stress-corrosion. However, it must be emphasized that this protective influence can anneal out during long time, elevated temperature exposures.

Cyclic Exposures

There have been several investigations reported in the literature (8-10) that have indicated time accumulated in short stress-corrosion exposure cycles is not as detrimental as continuous exposure for an equivalent total time. Since aircraft engines, especially military, usually operate for relatively short times, the 100 hour continuous exposure threshold curves commonly generated in laboratory tests represent conditions which are more severe than normal engine operating conditions. Previous investigations ranged from qualitative observations of crack formation to detailed analyses of corrosion products and their relation to the cycle times at both the temperature where stress-corrosion occurred and at room temperature. In all of these previous studies, only the exposure temperature was cycled while the stress applied to the specimens remained constant. The purpose of our investigation (11) was to more closely simulate the actual stress-

temperature profile of compressor components by cycling both stress and temperature. They were cycled independently to determine their individual effects and simultaneously to determine their combined effect.

Stress Cycling. A stress cycling threshold curve is shown in figure 3. Specimens were heated to the stress-corrosion exposure temperatures for a continuous period of 96 hours, while they were alternately stressed for 1 hour and unstressed for 3 hours. Hence, specimens were stressed for only 25 percent of the total stress-corrosion exposure period. It is evident that such a stress profile results in a substantially greater threshold stress at 320° C but no change in threshold stress at 430° C, when compared with the standard 96 hour continuous exposure threshold curve. The most likely role of stress in the process of hot-salt stress-corrosion of titanium alloys is to influence the diffusion and segregation of corrosion-produced hydrogen (12,13).

Temperature Cycling. Two temperature cycling threshold curves are also shown in figure 3. For one cycle, specimens were heated to the exposure temperatures for 1 hour and then allowed to cool for 1 hour. For the other cycle, the times were 1 and 3 hours, respectively. In both cases specimens were stressed continuously during temperature cycling and the total time at the exposure temperatures was a constant 96 hours. When the cooling time was only 1 hour, the threshold stress was significantly greater than the baseline at lower exposure temperatures. However, when the cooling time was 3 hours, threshold stresses over the entire range of exposure temperatures were approximately twice those determined for the baseline threshold curve.

It is evident from these two threshold curves that a relation exists between the cyclic exposure times at elevated temperatures and room temperature. Such increases in threshold stresses are consistent with increases in crack nucleation time reported previously (10). These previous investigators reported threefold increases in crack nucleation time if the exposure time at elevated temperatures was less than the time required to form the corrosion product titanium dichloride, or if the exposure time at room temperature was long enough to result in the decomposition of titanium dichloride. Room temperature hydrolysis of titanium dichloride has been suggested as a probable reaction (14).

Stress and Temperature Cycling. The combined effect of stress and temperature cycling is also shown in figure 3 by the uppermost threshold curve. This effect is barely evident at 320° C because of normal creep rupture limitations. It appears that at 430° C temperature cycling effects are dominant and there is no additional effect of the particular stress and temperature cycle studied here. It is possible that other combinations of stress-temperature profiles might result in increases in the crack threshold stress at 430° C.

Hydrogen Embrittlement

Corrosion-produced hydrogen has been shown to be the damaging species in the process of hot-salt stress-corrosion of titanium alloys. Specimens exposed to hot-salt stress-corrosion conditions exhibited both temperature and strain-rate sensitivity during subsequent tensile testing. Embrittlement after exposure was most severe in room temperature tensile tests at a low, constant cross-head speed of 0.01 cm/min. Embrittlement could be eliminated after exposure by vacuum annealing treatments which removed the hydrogen (12). Chemical analyses detected substantial increases in hydrogen content of stress-corroded specimens of all alloys tested (see Table I). Advanced analytical techniques (ion microprobe and laser microprobe) have proven that this corrosion-produced hydrogen is segregated in regions below the salt-corroded and fracture surfaces of embrittled alloy specimens. Concentrations of several thousand ppm were measured in 811 alloy specimens by both techniques. Typical results obtained with the ion microprobe are shown in figure 4 (15).

This confirmation of hydrogen concentrations of thousands of ppm at substantial depths below fracture surfaces is incompatible with stress-sorption or surface adsorption theories of hydrogen embrittlement. An internal hydrogen embrittling mechanism is undoubtedly responsible for hot-salt stress-corrosion embrittlement and cracking. It is suggested that the following sequence of events occurs during elevated temperature hot-salt stress-corrosion exposures. Corrosion-produced hydrogen diffuses to regions of high triaxial stress, such as corrosion pits and crack tips. The hydrogen enriched region is embrittled and cracks normal to the direction of applied stress. The crack will propagate through the embrittled region until it is blunted by plastic deformation in the ductile matrix. Further cracking requires additional diffusion of hydrogen and embrittlement of the region in front of the new crack tip. This sequential process can continue if sufficient hydrogen is supplied by the corrosion reactions occurring near the crack mouth and as long as the favorable conditions of high temperature and stress-induced diffusion are not interrupted.

The strain-rate and temperature sensitivity discussed above demonstrates that interstitially dissolved hydrogen is responsible for embrittlement observed during tensile testing after stress-corrosion exposures. Elevated temperature tensile tests of hydrogenated specimens (13), measured concentrations of several thousands of ppm of hydrogen (15), and recent unpublished hot-stage electron microscopy experiments suggest that titanium hydrides are present in the vicinity of stress-corrosion cracks. However, the mere presence of hydrides does not allow one to distinguish between hydrides and interstitial hydrogen as the embrittling form of hydrogen. Hence, it is not conclusively known which form of

hydrogen is responsible for embrittlement and cracking during elevated temperature stress-corrosion exposures.

Concluding Remarks

This investigation has demonstrated that the major variables influencing hot-salt stress-corrosion of titanium alloys are: 1. alloy processing conditions, heat-to-heat variations, and composition; 2. surface condition; and 3. cyclic exposures. Under simulated compressor environmental conditions the commonly used 64 alloy is creep limited and not stress-corrosion limited. Since most compressor components are shot-peened to increase fatigue resistance, these components also exhibit increased resistance to stress-corrosion. Cyclic exposures to stress-corrosion conditions are not as detrimental as continuous exposures for equivalent total times.

The process of hot-salt stress-corrosion is complex and may consist of the following interrelated stages: initial surface corrosion; hydrogen absorption and diffusion; embrittlement and crack propagation. It is probable that the effects of surface condition, alloy and phase composition are most significant in the process of initial surface corrosion. Hydrogen absorption is known to be affected by alloy composition and crystal structure. Processing and heat treating variables which affect alloy microstructure can exert an influence on both the hydrogen embrittlement characteristics and crack propagation or fracture toughness of the alloy. Cyclic stress-temperature exposures could influence all three stages of the process of stress-corrosion.

The major variables affecting susceptibility to hot-salt stress-corrosion determined in this investigation satisfactorily rationalize the current lack of service failures. However, there is still reason for concern that there may be some service failures as developmental engines call for newer, stronger alloys that may be susceptible to processing variables such as the 5621S. Such alloys would be intended for use at higher operating stresses and temperatures and for longer cyclic periods at peak thrust. Under such operating conditions the beneficial effects of both cyclic exposures and shot-peening would be reduced.

References

1. Stress-Corrosion Cracking of Titanium, ASTM STP 397, 1966.
2. Gray, H. R., Hot-Salt Stress-Corrosion of Titanium Alloys, Aerospace Structural Materials, NASA SP-227, 1970, pp. 251-268.
3. Ashbrook, R. L., A Survey of Salt Deposits in Compressors of Flight Gas turbine Engines, NASA TN D-4999, 1969.
4. Minkler, W. W., discussion of paper by Cotton, J. B., Stress Corrosion of Titanium Alloys, Stress Corrosion Cracking in Aircraft Structural Materials, AGARD Conf. Proceeding No. 18, 1967, pp. VI 1-20.
5. Gray, H. R., Relative Susceptibility of Titanium Alloys to Hot-Salt Stress-Corrosion, NASA TN D-6498, 1971.
6. Gray, H. R. and Johnston, J. R., Hot-Salt Stress-Corrosion of a Titanium Alloy in a Dynamic Air Environment, Metallurg. Trans., Vol. 1, no. 11, November, 1970, pp. 3101-3105.
7. Green, H. M. and Shamblen, C. E., General Electric Co., private communication.
8. Heimerl, G. J., Braski, D. N., Royster, D. M., and Dexter, H. B., Salt Stress Corrosion of Ti-8Al-1Mo-1V Alloy Sheet at Elevated Temperatures, Stress-Corrosion Cracking of Titanium, ASTM STP 397, 1966, pp. 194-214.
9. Piper, D. E. and Fager, D. N., The Relative Stress-Corrosion Susceptibility of Titanium Alloys in the Presence of Hot Salt, Stress-Corrosion Cracking of Titanium, ASTM STP 397, 1966, pp. 31-52.
10. Stone, L. H. and Freedman, A. H., Cyclic Hot-Salt Stress Corrosion of Titanium Alloys, Rep. NOR-67-151, Northrop Corp. (AFML-TR-67-289, AD-825239), Sept. 1967.
11. Gray, H. R., Effect of Cyclic Exposure on Hot-Salt Stress-Corrosion of a Titanium Alloy, NASA TN, to be published.
12. Gray, H. R., Hot Salt Stress Corrosion of a Titanium Alloy: Generation of Hydrogen and Its Embrittling Effect, Corrosion, Vol. 25, no. 8, August, 1969, pp. 337-341.
13. Gray, H. R., Role of Hydrogen in Hot-Salt Stress-Corrosion of a Titanium Alloy, Stress Corrosion Mechanisms in Titanium Alloys, NACE Symposium, 1972.

14. Rideout, S. P., The Initiation of Hot-Salt Stress Corrosion Cracking of Titanium Alloys, Applications Related Phenomena in Titanium Alloys, ASTM STP 432, 1968, pp. 205-217.

15. Gray, H. R., Ion and Laser Microprobes Applied to the Measurement of Corrosion Produced Hydrogen on a Microscopic Scale, Corrosion, Vol. 28, 1972.

TABLE I. - VENDOR CERTIFIED CHEMICAL ANALYSES OF TITANIUM ALLOYS (WEIGHT PERCENT)

Alloy	Al	Sn	Zr	Mo	V	Si	Cr	Co	Fe	N	C	O	H	H ^a
811	7.8	---	---	1.0	1.0	---	---	---	0.05	0.011	0.023	0.07	0.0070	0.0100-0.0255
64	6.4	---	---	---	4.1	---	---	---	.13	.015	.021	.14	.0050	.0077- .0117
6242	6.3	2.0	3.8	2.0	---	---	---	---	.07	.009	.01	.098	.0070	.0103- .0153
679	2.3	10.7	4.7	1.1	---	0.18	---	---	.06	.008	.023	.14	.0066	.0109- .0137
5621S(1)	5.0	6.4	1.9	.92	---	.28	---	---	.03	.006	.02	.10	.0056	---
5621S(2)	5.2	5.9	1.9	.84	---	.27	---	---	.05	.009	.02	.113	.0036	.0063- .0192
643	6.5	---	---	---	3.9	---	---	3.3	.05	.012	---	.15	.0147	.0177- .0207
13-11-3	3.0	---	---	---	13.4	---	10.5	---	.13	.026	.018	.12	.0104	.0269- .0302

^aHydrogen contents of stress-corroded specimens.

TABLE II. - HEAT TREATMENTS AND MICROSTRUCTURES

Alloy	Heat treatment	Microstructure, pct of phases
811 Mill annealed/air cool	As-received (790° C, 1 hr, air cool)	7 Equiaxed β - 93 continuous primary α
811 MA/furnace cool	MA/AC + 900° C, 1 hr, furnace cool	7 Equiaxed β - 93 continuous primary α
811 Duplex	MA/AC + 650° C, 24 hr, AC	7 Equiaxed β - 93 continuous primary α
811 Triplex	MA/AC + 1010° C, 1 hr, AC + 590° C, 8 hr, AC	50 Equiaxed primary α - 50 continuous transformed β
64 Mill annealed	As-received (840° C, 2 hr, FC to 700° C, 2 hr, AC)	10 Equiaxed β - 90 continuous primary α
64 Duplex	MA + 930° C, 1 hr, water quench + 540° C, 4 hr, AC	50 Equiaxed primary α - 50 continuous transformed β
6242 Mill annealed	As-received (900° C, 1 hr, AC)	7 Equiaxed β - 93 continuous primary α
6242 Duplex	MA + 970° C, 1 hr, AC + 590° C, 8 hr, AC	60 Equiaxed primary α - 40 continuous transformed β
679 Mill annealed	As-received (700° C, 2 hr, AC)	5 Equiaxed β - 95 continuous primary α
679 Duplex	MA + 900° C, 1 hr, AC + 500° C, 24 hr, AC	50 Equiaxed primary α - 50 continuous transformed β
5621S(1)	As-received (980° C roll, 980° C, 1 hr, AC + 590° C, 2 hr, AC)	10 Equiaxed primary α - 90 continuous transformed β
5621S(2A)	As-received (980° C roll, 1040° C, 1 hr, AC + 590° C, 2 hr, AC)	100 Transformed β (Widmanstätten)
5621S(2B)	As-received (1040° C roll, 1040° C, 1 hr, AC + 590° C, 2 hr, AC)	100 Acicular transformed β
5621S(2C)	(2B) + 980° C, 1 hr, AC + 590° C, 2 hr, AC	100 Acicular transformed β
643 Duplex	840° C, 1 hr, WQ + 480° C, 2 hr, AC	30 Equiaxed primary α - 70 continuous β
13-11-3 Duplex	As-received (790° C, 1/4 hr, WQ + 480° C, 22 hr, AC)	90 Metastable β - 10 decomposition phases (α , ω , . . .)

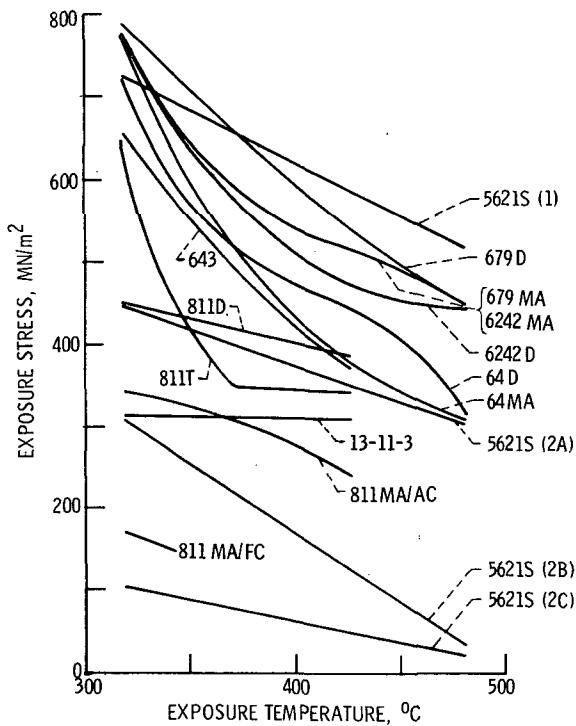


Figure 1. - 96-Hour crack threshold curves for chemically-milled specimens of titanium alloys (see tables I and II for compositions and heat treatments).

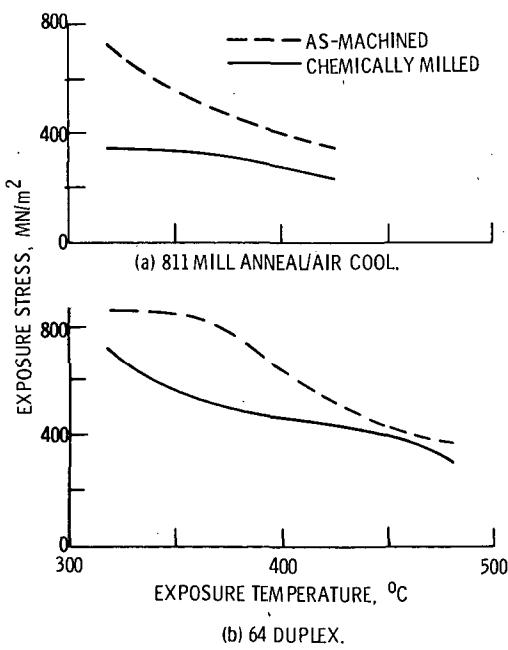


Figure 2. - 96-Hour crack threshold curves for as-machined and chemically milled specimens.

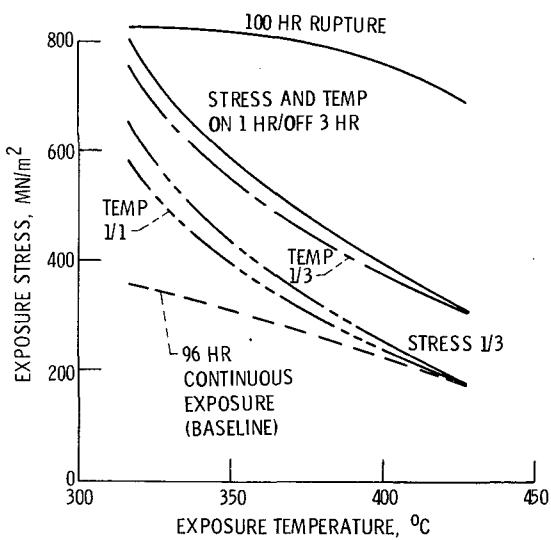


Figure 3. - Cyclic exposure crack threshold curves for chemically milled specimens of 811 mill anneal/air cool alloy.

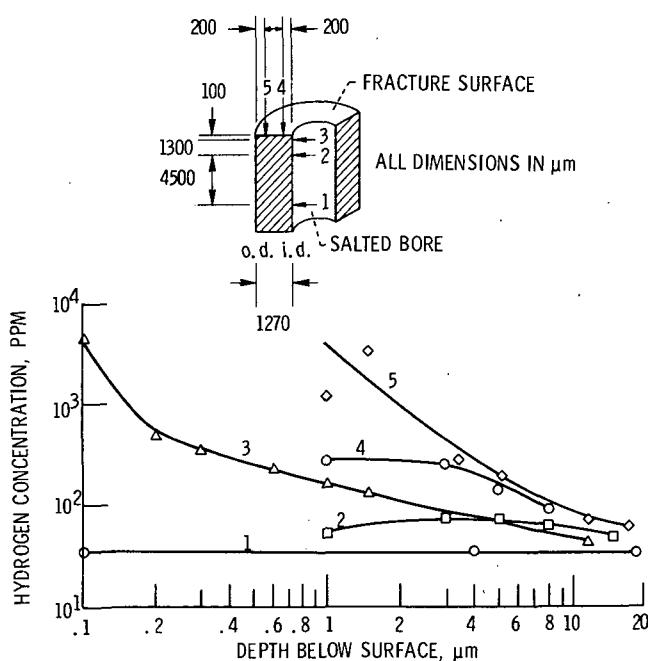


Figure 4. - Ion microprobe hydrogen concentration profiles for stress-corroded 811 mill anneal/air cool alloy specimen.